PFM studies of ferroelectric phase transition in superprotonic $(K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2$ crystals

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Crystals $M_mH_n(AO_4)_{(m+n)/2}\cdot yH_2O$ (M = K, Rb, Cs, NH_4, AO_4 = SO_4, SeO_4, HPO_4, $HAsO_4$) are of special interest as a potential material for the creation of various electrochemical devices. The proton conductivity is important characteristic of these crystals. Study of temperature behavior of $(K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2$ crystals at cooling and detection of phase transitions by PFM methods are purpose of this work.

The photo of $(K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2$ crystals, grown in the Institute of Crystallography, are shown in Figure 1a. Crystals were grown in the $K_3H(SO_4)_2$–$(NH_4)_3H(SO_4)_2$– H_2O system [1]. In contrast to the known members of $M_3H(AO_4)_2$ family that have a superprotonic phase transition with an increase in symmetry from monoclinic to trigonal at heating, the crystals of $(K,NH_4)_3H(SO_4)_2$ with 57% of ammonium grow in the superprotonic phase [2]. X-ray study shows that crystals has trigonal symmetry, space group $R\overline{3}$, $Z = 3$, $a = b = 5.7768(3)$, $c = 22.0983(1)$ Å at $T \approx 23$ C. The trigonal symmetry is conditioned by the K/N occupation ratio and corresponding coordination of NH_4 groups (Fig. 1b). The appearance of the threefold axis leads to disordering of the O atoms involved in hydrogen bonds and as a result to the formation of a dynamically disordered network of hydrogen bonds, and rise of conductivity.

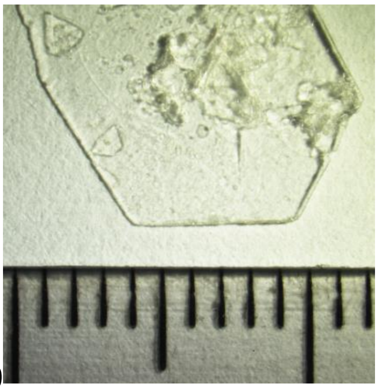
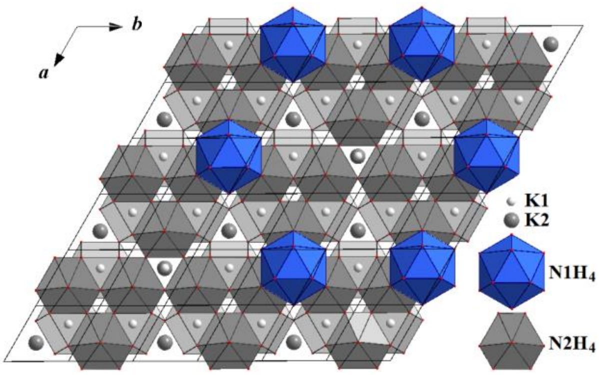
(a)  (b) 

Figure 1. (a) $(K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2$ crystals. (b) model of the arrangement of K and N atoms in $(K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2$ crystals: K1 atoms and $N1H_4$ coordination polyhedra, located in the layers of SO_4 tetrahedra, and K2 atoms and $N2H_4$ coordination polyhedra, located between the layers, are shown. SO_4 tetrahedra and hydrogen bonds are omitted.

The $(K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2$ crystal was investigated with two PFM methods using various ways of registration the piezoelectric response. The first one is traditional contact PFM, the second – hybrid PFM. The PFM measurements were carried out with scanning probe microscope NTEGRA Prima (NT-MDT Spectrum Instruments) using NSG01/Pt tip. Also the temperature controller MP6LC which allows to vary temperature (T) from -30 °C to +120 °C was used. The maximum interaction force between tip and surface was 160 nN. The temperature varied three times: from 23 ± 0.1 °C to 5 ± 0.1 °C and backwards.

Figure 2 demonstrates the structural changes in the crystal, which occur with a decrease in temperature from 23 °C to 5 °C. Fig. 2a shows the relief of a polished (001) crystal surface. The PFM image (Fig. 2b) shows that at $T = 23$ °C the crystal was in the paraphase. With a decrease in temperature to 9 °C, a transition to the ferroelectric state was observed (Fig. 2c). Small domains with the size about 1 μm are visible on monodomain area. Measurement of mechanical properties allows to observe the small areas with hardness lower than the main template hardness (Fig. 2d). With the temperature decrease to 5 °C, no changes in the structure were observed (Fig. 2e). Repeated temperature change in the range of 5-23 °C showed that the phase transition is reversible.

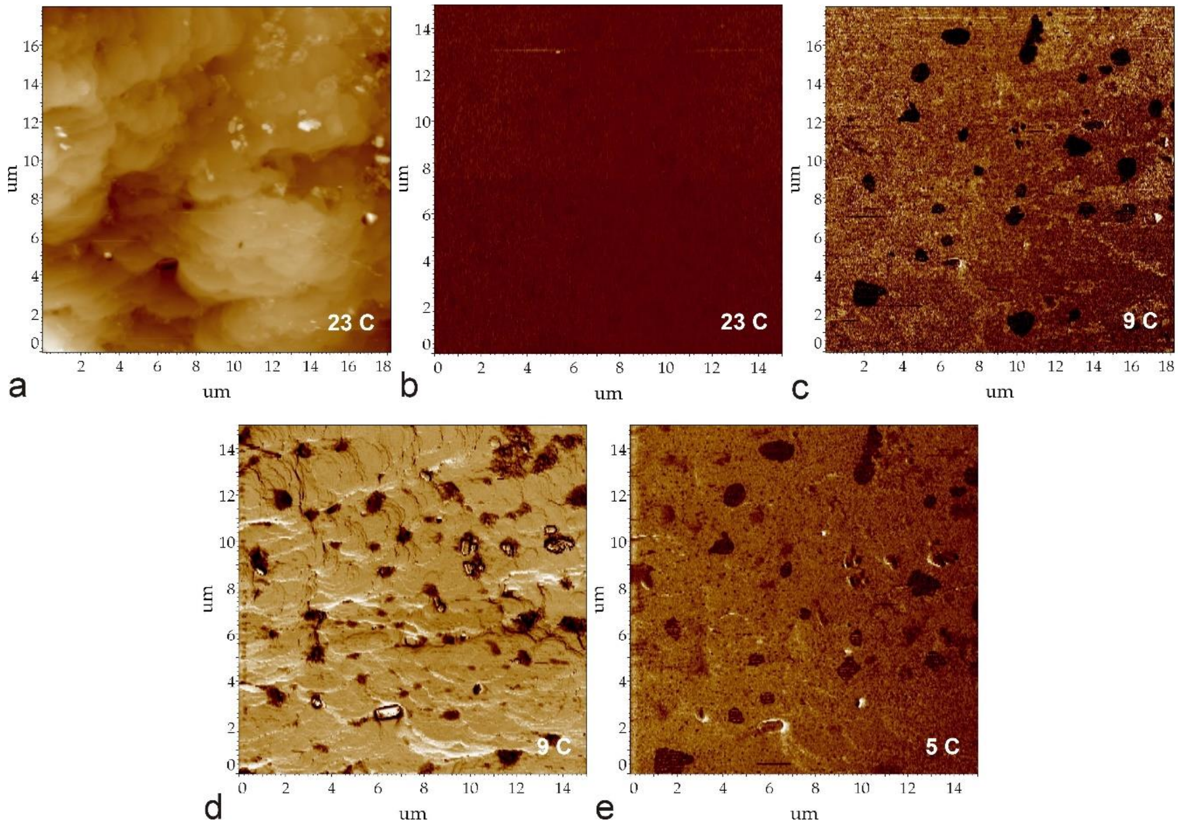


Figure 2. AFM images of $(K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2$ crystal as a function of temperature: (a) topography, contact AFM; (b, c, e) contact in-plane PFM (phase); (d) hybrid mode, hardness (arb. un.).

The PFM method allows first time to observe the phase transition (from paraphase to ferroelectric phase) in $(K_{0.43}(NH_4)_{0.57})_3H(SO_4)_2$ crystal with temperature decrease. The obtained information supplements the structural and dielectric data [2].

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